

# Double Melting Phenomena of Polyphenylene Sulfide and Its Blends

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## SYNOPSIS

The melting behavior of PPS (polyphenylene sulfide) and its blends with PSF (bisphenol A polysulfone) and PEK-C (polyetherketone with phthalidylidene groups) are investigated with DSC technique. It is found that, with a rise in melt temperature  $T_{\text{melt}}$  and melt time  $t_{\text{melt}}$ , the intensities of the lower melting peaks of PPS increase while those of the upper ones decrease or disappear in some cases, which can be attributed to the obstructive effect of branching or crosslinking of PPS macromolecules on the crystallization of PPS at higher temperature. As the annealing crystallization temperature increases, both the peak temperatures and intensities of the lower melting peaks of PPS increase. PSF and PEK-C have no influence on the lower melting peaks of PPS but are unfavorable to the crystallization of the higher melting species. The double melting behavior of the PPS component in the blends is much more susceptible to the changes in  $T_{\text{melt}}$  and  $t_{\text{melt}}$  than that of neat PPS. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

PPS (polyphenylene sulfide) is a semicrystalline thermoplastic polymer provided with excellent mechanical properties, thermal resistance, and heat stability, and has been used widely as a matrix resin in high performance composites. In most cases, however, neat PPS of higher crystallinity is very brittle so that its application is restricted. Recently, efforts have been made on toughening PPS by blending with high performance thermoplastics in hopes of improving toughness of PPS while maintaining other properties.<sup>1-5</sup> The results revealed that all these blends are incompatible systems and the toughness of PPS could be improved to a certain extent.

One of the important characteristics of PPS lies in its solid-state reaction capacity. In the process of heat treatment under certain conditions, chain growth, branching, and crosslinkage might occur with PPS macromolecules. Therefore, properly heat-treated blends of PPS with high performance ther-

moplastics could form a so-called semi-IPN (semi-interpenetrating polymer network) and acquire optimum performance. Significant progress has been extended over the past years in toughening brittle thermosetting resin on the basis of the concept of semi-IPN.<sup>6-9</sup> The authors of the present paper have studied systematically the PPS blends with two high performance thermoplastic polymers: PSF (bisphenol A polysulfone) and PEK-C (polyetherketone with phthalidylidene groups), with the objective to their application as tough materials. The aim of the present paper is focused on the double melting behavior of PPS in blends as well as of neat PPS, and the influence of the thermoplastics on the melting behavior of PPS in blends.

## EXPERIMENTAL

**Sample Preparation.** PSF with reduced viscosity 0.48 kindly supplied by the Shanghai Shuguang Chemical Plant (China) and PEK-C with reduced viscosity 1.1 produced by the Xuzhou Engineering Plastics Plant (China) were dissolved in 1,2-dichloroethane to make 5% solutions, respectively. Powdered PPS (sieved through 40 mesh/in.<sup>2</sup>) with a

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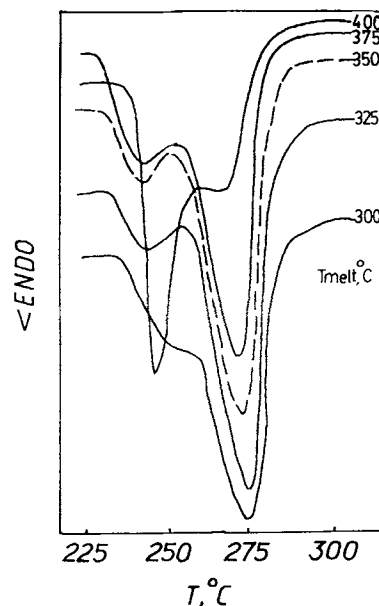
number average molecular weight of 2200 g/mol produced by the Changshou Chemical Plant (China) was mixed in the solutions uniformly. Then, the suspensions were poured onto clean glass plates, allowing evaporation of the solvent at room temperature. Finally, these binary or ternary filmy samples with various compositions were removed from the glass plates and dried in vacuum at 120°C for 3 h.

**DSC Measurements.** PPS and its blends were melted completely under various conditions in a mode CDR-1 differential scanning calorimetry made by the Shanghai Balance Instrument Factory (China), and quenched in cold water. Then, the quenched samples were annealed in DSC for a certain period of time and cooled again in air. DSC scans were carried out, followed, and recorded at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### The Influence of Melt Temperature $T_{melt}$ on the Double Melting Behavior of Neat PPS

There has been a lot of research on the melting behavior of PPS,<sup>10-15</sup> especially on the origin of its double melting peaks, which were similarly observed in PEEK (polyetheretherketone),<sup>16-18</sup> PI (polyimide),<sup>19</sup> and PET (polyethylene terephthalate),<sup>20</sup> and other semicrystalline homopolymers. Chung and Cebe found triple melting peaks in the PPS of low molecular weight.<sup>15</sup> In order to explain the phenomenon of this kind, several models have been proposed. Some attributed it to the presence of two sorts of crystalline or crystalline morphology,<sup>21-23</sup> and some suggested it should result from the melt, recrystallization, and subsequent remelt of the crystalline species with lower melting point.<sup>12-18,20,24</sup> Wunderlich and coworkers regarded that the higher melting peak is due to the melting of the primary lamellae and the lower one is the result of the melting of the imperfect crystals.<sup>16</sup> The experimental data of Budgell and Day<sup>10</sup> indicated that a higher melt temperature  $T_{melt}$  led to a rise in peak height of the lower melting peak and its fusion heat  $\Delta H_{m1}$ , but a drop in the peak intensity of the upper melting peak, and moreover, the peak temperature of the upper melting peak,  $T_{m2}$ , did not change with increasing  $T_{melt}$ . They considered that this meant some portion of the higher melting species had degraded but retained the ability to partially crystallize, and must not be the result of an increase in molecular weight caused by crosslinking or chain extension of the lower melting species.<sup>10</sup>



**Figure 1** Effect of melt temperature  $T_{melt}$  on the melting behavior of PPS.  $T_a = 220^\circ\text{C}$ ,  $t_a = 3$  h, and  $t_{melt} = 10$  min.

Figure 1 shows the melting peaks of the quenched PPS which was annealed at 220°C subsequently for 3 h. The curves illustrated that all the PPS samples treated under the given conditions exhibit double melting peaks. In the case of the same annealing temperatures and times,  $T_{melt}$  exerts great influence on the peak intensities of the lower melting peaks but nearly not on their peak temperatures  $T_{m1}$  (in Table I,  $T_{m1}$  is confined to having a concern with the annealing temperature  $T_a$ :  $T_{m1}$  increases as  $T_a$  increases). On the other hand, it is found that there is a particular value for  $T_{melt}$ ; *i.e.*, 375°C in the case of neat PPS, below which  $T_{m2}$  is nearly not affected by  $T_{melt}$ . When  $T_{melt} \geq 375^\circ\text{C}$ , with increasing  $T_{melt}$ , the peak intensities and temperatures of the upper melting peaks decrease obviously, but the peak intensities of the lower melting peaks increase.

Although the description of the equilibrium melting point of PPS differs from one another,<sup>10-14</sup> it should be in the range from 301 to 357°C. In fact, whether  $T_{melt}$  has influence on the melting behavior of PPS crystalline region depends upon whether self-nucleation, branching, crosslinking, and degradation take place in PPS. A  $T_{melt}$  lower than the equilibrium melting point of PPS would leave unmelted PPS fragments with higher melting temperature, which could act as nucleating agents in the course of crystallization and form the crystals, presenting themselves as higher melting peak in DSC traces. Thus,  $T_{m2}$  has no relation to  $T_{melt}$ . A  $T_{melt}$  above the equi-

**Table I** Effect of Melt Temperature (°C) and Annealing Temperature (°C) on the Transition Temperatures (°C) of Neat PPS and Its Blends<sup>a</sup>

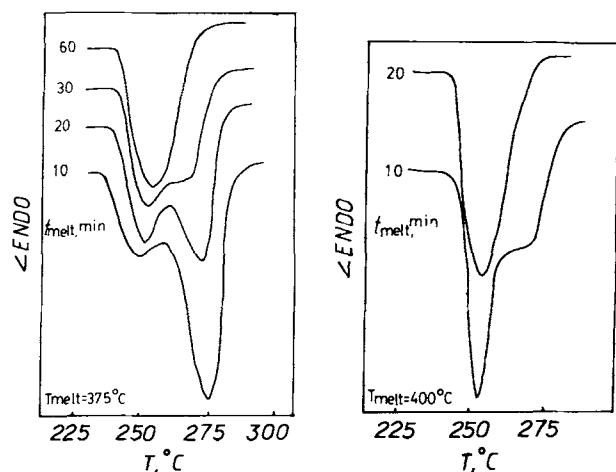
$T_{\text{melt}}$	$T_a$	PPS			PSF/PPS = 2/8			PSF/PPS = 4/6			PSF/PEK-C/PPS = 1/1/8		
		$T_{m1}$	$T_{m2}$	$T_c$	$T_{m1}$	$T_{m2}$	$T_c$	$T_{m1}$	$T_{m2}$	$T_c$	$T_{m1}$	$T_{m2}$	$T_c$
300	210	243	275	228	237	275	217	239	272	209	242	275	216
	220	252	276	224	251	271	216	250	268		252	273	210
	230	260	274	230	258	270	195	260	269	199	261		
325	210	236	275	229	236	275	222	238	275	204	235	272	220
	220	245	274	230	249	275	218	247	273	211	248	270	206
	230			225	258	275	216	259	270	189	259	272	208
350	210	233	275	226	242	258		243	260		242	256	
	220	246	273	228	249	260		251			253		
	230	256	276		255			257			258		
375	210	235	270	193									
	220	248	273	202									
	230	255	274	208									
400	210	238	263	166									
	220	250	267	172									
	230	256	269	188									

<sup>a</sup>  $t_{\text{melt}} = 10$  min and  $t_a = 3$  h.

librium melting point of PPS, however, would lead to complete melting and branching or crosslinking in PPS, which destroys the ordered structure of PPS to some extent so that only less perfect crystals could be obtained, i.e., the peak intensity and temperature of the higher melting peak are reduced when  $T_{\text{melt}}$  reaches 400°C. On the other hand, PPS with lower ordering structure caused by branching or crosslinking could continue to have crystallization capacity and form a great number of crystals of lower melting temperature in the process of annealing. Budgell and Day stated that thermal degradation during melting at high melt temperature was responsible for the less perfect crystalline species of lower melting temperature.<sup>10</sup> Supposing their analysis is right, the lower melting polymer crystals ought to reorganize and form higher melting crystalline species during annealing, but the higher melting peak is factually not so evident as expected. That is to say, the explanation of the effect of  $T_{\text{melt}}$  on double melting peaks in the light of chain branching or crosslinking seems to be more rational. This coincides with the fact that the cooling crystallization temperature  $T_c$  decreases with increasing  $T_{\text{melt}}$ —higher  $T_{\text{melt}}$  facilitates branching or crosslinking.

### The Influence of Melt Time $t_{\text{melt}}$ on the Double Melting Behavior of Neat PPS

Figure 2 illustrates the melting behavior of the PPS samples which were melted at 375 and 400°C for various periods of time respectively and quenched prior to annealing at 220°C for 3 h. It is clear that, with increasing melt time  $t_{\text{melt}}$ , the upper melting peaks are so diminished that they merge with the lower melting peaks. Also, the dependence of the lower melting peaks on  $t_{\text{melt}}$  goes quite the contrary: the intensity increases more and more obviously as  $t_{\text{melt}}$  increases. The higher  $T_{\text{melt}}$ , the more significant the tendency. This phenomenon has not been reported in the literature till now, and can be explained in the light of branching or crosslinking. Longer  $t_{\text{melt}}$  might result in higher degree of branching or crosslinking of PPS and a smaller amount of the perfect crystalline, i.e., there would be a rise in the amount of the imperfect crystals formed during annealing. Owing to the hindrance of branched and crosslinked structures to crystallization, the imperfect crystalline species could not be reorganized and transformed into crystals of more perfect structure. For higher melt temperature  $T_{\text{melt}}$ , the degree of branching or crosslinking of PPS would also be increased



**Figure 2** Effect of melt time  $t_{\text{melt}}$  on the melting behavior of PPS.  $T_a = 220^\circ\text{C}$  and  $t_a = 3$  h.

so that the upper melting peak disappear within a shorter period of  $t_{\text{melt}}$  and only a single melting peak—the lower melting peak could be observed.

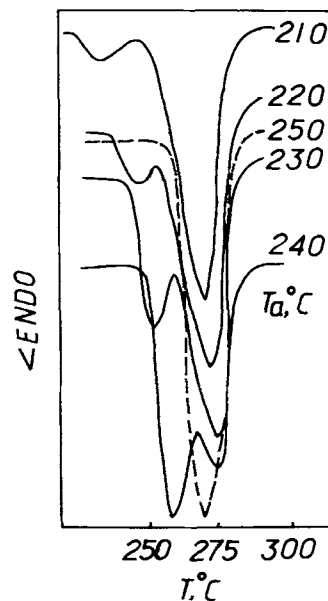
### The Influence of Annealing Conditions on the Double Melting Behavior of Neat PPS

In the field of research on the double melting behavior of semicrystalline polymers, most interests used to be concentrated upon the influence of annealing conditions. It has been reported that, with a rise in annealing temperature  $T_a$ ,  $T_{m1}$  shifts to higher temperature and  $T_{m2}$  remains unchanged below a certain  $T_a$ . Besides these phenomena, Figure 3 shows that, with increasing  $T_a$ , the intensities of the lower melting peaks increase and become superior to those of the higher melting peaks, or the two peaks merge into a single peak when  $T_a$  exceeds a critical value. In fact, lower  $T_a$  means higher degree of supercooling, which leads to a greater number of the active crystalline seeds of higher melting temperature. After annealing, the crystalline species of higher melting temperature constitute the majority with respect to the total degree of crystallinity. With a rise in  $T_a$ , the crystal nucleating density of the less perfect crystallines of lower melting temperature increase so that these crystalline species make more of a contribution to the total degree of crystallinity and exhibit higher peak height during DSC scanning in comparison with the upper melting peaks. When  $T_a$  increases and exceeds a certain temperature, the degree of perfection of the crystalline of lower melting temperature becomes almost the same as that of the crystalline of higher melting temperature. So, only a single peak comes into existence. The degree

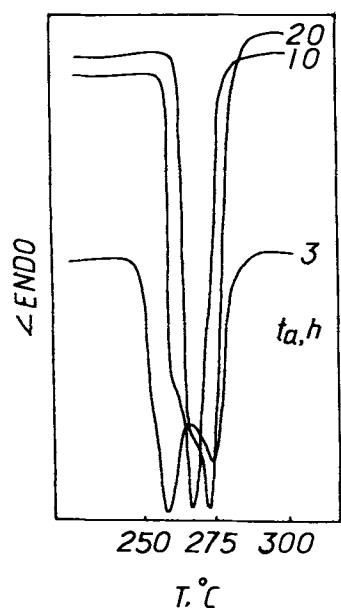
of perfection of the crystalline of lower melting temperature is also increased as annealing time  $t_a$  increases, which is confirmed by the fact that  $T_{m1}$  increases with increasing  $t_a$  (Fig. 4).

### The Influence of Thermoplastics on the Double Melting Behavior of Neat PPS

The melting behaviour of the PPS blends with PSF and PEK-C are shown in Figure 5. The samples were melted at 300 and 350°C for various periods of time, respectively, and subsequently annealed at 230°C for 3 h. Double melting peaks are observed in neat PPS, PSF/PPS = 20/80, and PEK-C/PPS = 20/80; however, the peak shape differs from one another. The peak heights of the upper melting peaks of neat PPS are higher than those of the lower ones, and the incorporation of PSF and PEK-C results in a drop in the intensities of the upper melting peaks of PPS but a rise in the peak heights of the lower melting peaks. When the contents of PSF and PEK-C are 40 wt %, the upper melting peaks of PPS disappear (for PEK-C/PPS = 40/60) or act as a peak shoulder at the higher temperature side of the lower melting peak. On the other hand, Figure 5 indicates that PSF and PEK-C exert different influences on the double melting behavior of PPS. Owing to the fact that  $T_g$  and viscosity of PEK-C is higher than those of PSF, PEK-C affects the melting behavior of PPS much more significantly. When  $T_{\text{melt}}$  ap-



**Figure 3** Effect of annealing temperature  $T_a$  on the melting behavior of PPS.  $t_a = 3$  h,  $T_{\text{melt}} = 350^\circ\text{C}$ , and  $t_{\text{melt}} = 10$  min.

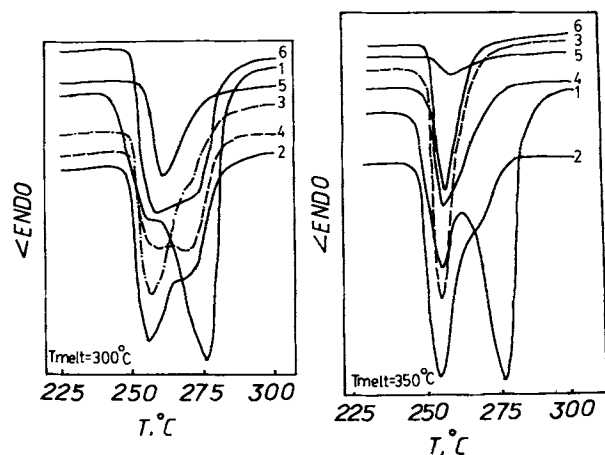


**Figure 4** Effect of annealing time  $t_a$  on the melting behavior of PPS.  $T_a = 240^\circ\text{C}$ ,  $T_{\text{melt}} = 350^\circ\text{C}$ , and  $t_{\text{melt}} = 10$  min.

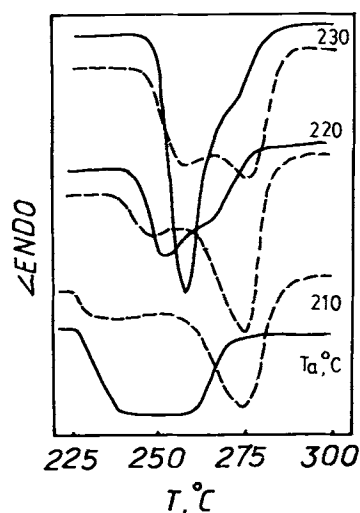
proaches  $350^\circ\text{C}$ , branching and crosslinking in PPS become more frequent. Only a peak shoulder can be seen at the high temperature side of the lower melting peak in the DSC trace of PSF/PPS = 20/80, and there is no upper melting peak for PEK-C/PPS = 20/80. With increasing the content of PSF and PEK-C, there are only single peaks—lower melting

peaks appear in the DSC trace of PPS in the blends. The crystal melting behavior of PPS in the triple blends exhibits an intermediate feature between PSF/PPS and PEK-C/PPS. It is evident that both PSF/PPS and PEK-C/PPS retard the crystallization of upper melting crystals of PPS. The higher  $T_{\text{melt}}$ , the more remarkable the retardation effect due to the fact that both PSF and PEK-C are of higher glass transition temperature  $T_g$  ( $= 190$  and  $225^\circ\text{C}$ , respectively); they could impede the diffusion of PPS segments into crystal nuclei during annealing and the reorganization of the lower melting crystals to transform into higher melting species in the heating process of DSC scanning. So the upper melting peaks of PPS in the blends not only tend to be reduced, but also disappear for higher  $T_{\text{melt}}$  because of the enhanced interaction between PPS and the thermoplastics.

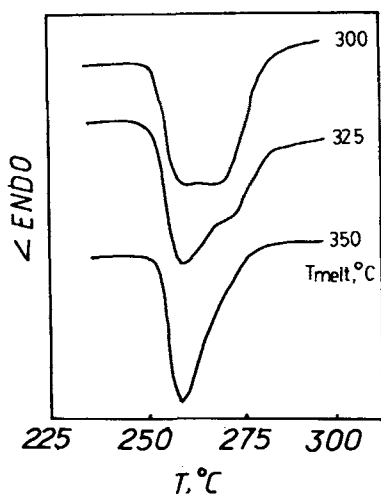
Figures 6 and 7 show the effect of melting temperatures and annealing temperatures on the melting behavior of PPS blends. When  $T_{\text{melt}}$  is  $320^\circ\text{C}$ , double melting peaks can be observed in blend; and, with a rise in  $T_a$ ,  $T_{m2}$  remains unchanged but  $T_{m1}$  shifts to higher temperature. When  $T_{\text{melt}}$  is  $350^\circ\text{C}$ , the double melting peaks of PPS in PSF/PPS (20/80) merge into a single lower melting peak, gradually with increasing  $T_a$ ; besides, the same phenomenon also takes place in PEK-C/PPS (20/80) when  $T_{\text{melt}}$  increases. It is noteworthy that not only the thermoplastics with high  $T_g$  but also the melting and annealing conditions exert influence on the melting behavior of PPS component in the blends.



**Figure 5** Effect of melt temperature  $T_{\text{melt}}$  on the melting behavior of PPS and its blends.  $t_{\text{melt}} = 10$  min,  $T_a = 230^\circ\text{C}$ , and  $t_a = 3$  h. (1) PPS; (2) PSF/PPS = 20/80; (3) PSF/PPS = 40/60; (4) PEK-C/PPS = 20/80; (5) PEK-C/PPS = 40/60; (6) PSF/PEK-C/PPS = 10/10/80.



**Figure 6** The melting behavior of the PSF/PPS (= 20/80) sample. (---)  $T_{\text{melt}} = 325^\circ\text{C}$ ; (—)  $T_{\text{melt}} = 350^\circ\text{C}$ ;  $t_{\text{melt}} = 10$  min and  $t_a = 3$  h.



**Figure 7** The melting behavior of the PEK-C/PPS (= 20/80) sample.  $t_{\text{melt}} = 10$  min,  $T_a = 230^\circ\text{C}$ , and  $t_a = 3$  h.

## CONCLUSION

The double melting behavior of PPS depends upon the melting and annealing conditions. With increasing melt temperature  $T_{\text{melt}}$  and melt time  $t_{\text{melt}}$ , the intensities of lower melting peaks increase, but those of upper ones decrease or disappear. These phenomena could be attributed to the branching and crosslinking structure of PPS which impede the formation of upper melting crystals and the transformation of lower melting crystals into upper melting crystals. With a rise in annealing temperature  $T_a$ , the higher melting peaks remain unchanged, but the peak temperature and peak height of the lower ones increase. In the case of  $T_a = 250^\circ\text{C}$ , the two peaks merge into one. The incorporation of thermoplastic PSF and PEK-C results in a drop in the peak height and peak temperature of upper melting peaks of the PPS component. The intensity of lower melting peaks of PPS increase with the addition of PSF and EK-C, but the peak temperature remains almost unchanged. It is evident that PSF and PEK-C retard the crystallization of upper melting crystals of PPS and the transformation of lower melting crystals into upper melting crystals. The higher  $T_{\text{melt}}$  or the longer  $t_{\text{melt}}$ , the more significant the changes in the melting behavior of PPS component in the blends.

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